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31102-11-3110540

## UNPUBLISHED PRELIZINARY DATA

# POLYMER DECOMPOSITION INITIATED BY HIGH ENERGY RADIATION

Prepared by Leo A. Wall

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PROGRESS REPORT
Covering Period:
June 1964 to February 1965

to

National Aeronautics and Space Administration Washington, D. C.

NASA Contract R-56

## POLYMER DECOMPOSITION INITIATED BY HIGH ENERGY RADIATION

Participating Investigators:

L.A. Wall R.E. Florin S. Straus H. Yu

#### 1. INTRODUCTION

The area of investigation of concern for this project is the changes, usually degradative, of polymer structure and properties resulting from exposure to vacuum ultraviolet and gamma radiation and at temperatures up to 500 or 600°C. For a profound insight into these effects, one needs a clear knowledge of the chemical and physical mechanisms involved. Numerous measurements as a function of time and conditions, of molecular weight, the rate of volatilization, the rate of stress relaxation, composition changes and various spectra on well characterized polymers are required.

#### 2. SUMMARY OF RECENT PROGRESS

- A) Construction and testing of vacuum ultraviolet lamps has continued using various power supplies and electrode arrangements in conjunction with a recording electrobalance.
- B) Thermolytic rates of volatilization have been completed on one study of polystyrene, see publication (\$), and a new program planned in which the rates of volatilization

of polystyrene with known end groups and of the monodispersed type will be investigated. In the meantime a brief investigation of a special anionically prepared poly-1,2-dihydronapthalene have been studied. The results of the study are somewhat unusual in that the material showed increasing rates of volatilization as its surface area decreased.

- C) An investigation of the rates of volatilization, sensitized by gamma rays, of polytetrafluoroethylene has been completed and a final manuscript prepared (see publication 7). Further work using other polymers is planned.

  A new apparatus for this study using a recording balance is under construction which will enable studies to be made on a greater variety of polymers and with greater accuracy. The method used so far has been strictly only applicable to polymers which decompose to give only monomer.
- D) One phase of the radiolytic stress relaxation studies has been completed (see publication 8). Recently the thermolytic stress-relaxation of a 70:30 ethylene-propylene copolymer has been measured in a vacuum as a function of temperatures (236 to 310°C). An activation energy of 42 kcal/mole was obtained for the scission reaction. Investigation of the influence of copolymer composition on the thermolytic stress-relaxation is now in progress.

#### 3. FUTURE PLANS

### Investigate:

- 1) Rates of radiation sensitized volatilization of various polymers.
- 2) Sensitization of polymers, for example, polyacrylonitrile, towards volatilization by prior irradiation.
- 3) Quantitative estimate of the molecular weight distribution of linear polyethylene and other vinyl polymers from the radiolytic stress relaxation, the elasticity measurements, the gel dose, and the number average molecular weight to test the theoretical predications set forth in publication (8).
- 4) Effect of substituents on the thermolytic chain scission of vinyl polymers observed by the stress relaxation of the networks in vacuum and in scavenging gases.
  - 4. SUMMARY OF PUBLICATIONS ON THIS PROJECT
- 1. "Pyrolysis of New Fluoropolymers", by S. Straus and L.A. Wall, SPE Trans. 4, [1], 56 (Jan. 1964).
- 2. "Pyrolysis of Polytrifluoroethylene. Influence of Gamma Radiation and Alkali Treatment", S. Straus and L.A. Wall, SPE Trans. 4, [1], 61 (Jan. 1964).
- 3. "Pyrolysis of Vinyl and Vinylidene Fluoride Polymers-Influence of Prior Gamma Irradiation", L.A. Wall, S. Straus,
  and R.E. Florin, manuscript submitted to J. Polymer Sci.

- 4. "Stress Relaxation of Fluorocarbon Elastomers During Gamma Irradiation", by T. Yoshida, R.E. Florin, and L.A. Wall, paper presented at the 144th American Chemical Society Meeting, Los Angeles, California, April 1963, manuscript accepted by J. Polymer Sci.
- 5. "On the Measurement of Random Chain Scission by Stress Relaxation", by Hyuk Yu, Polymer Letters 2, [4], 631 (1964).
- 6. "Effects of Composition and Irradiation on the Glass Transition Temperature of Methyl Methacrylate Styrene Copolymers", by M.S. Parker, V.J. Krasnansky and B.G. Achhammer, J. Appl. Polymer Sci. 8, 825 (1964).
- 7. "Gamma Ray Initiated Thermal Decomposition of Polytetra-fluoroethylene", by R.E. Florin, M.A. Parker, and L.A. Wall, manuscript in review.
- 8. "Radiolytic Stress Relaxation of an Ethylene-Propylene Copolymer", by H. Yu and L.A. Wall, manuscript submitted to J. Phys. Chem.
- 9. "The Thermal Degradation Mechanism of Polystyrene", by
  L.A. Wall, S. Straus, J.H. Flynn, D. McIntyre, and R. Simha,
  manuscript in review.
- 10. "The Effect of Gamma Irradiation on a Polyamide", by V.J. Krasnansky, M.S. Parker, and R.E. Florin, manuscript in review.